

SILANOL NETWORKS IN ZEOLITES INVESTIGATED WITH SOLID-STATE NMR

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ABSTRACT

The amount and location of acid sites (strong Brønsted and weak silanols) in zeolites are crucial for their applications. In this work we investigate the complex H-bonded silanol networks in MFI-type zeolites using solid-state NMR combined with DFT calculations. The spectral signatures are disclosed based on the experimental and theoretical correlations.

Key words: Solid-state NMR, silanol defects, Brønsted acid sites, DFT.

INTRODUCTION

The activity of zeolites resides in special hydroxyl groups present within their frameworks: the Brønsted acid sites (BAS) present at the oxygen bridge between Si and Al atoms ($\equiv\text{Si-OH-Al}\equiv$). Other hydroxyl groups, less acidic, exist in zeolites: the silanols, adjacent to Si atoms ($\equiv\text{Si-OH}$) inside the channels or on the solid's surface. The former ones are still a hot topic and several recent researches attempted their localization. The latter, are gaining a lot of interest lately since they permit the engineering of well-known zeolite structures to functionalize them or improve their catalytic performances. They are also identified as deactivation sites being sensitive to moisture and trappers of coke leading to low stability and short catalyst lifetime [1].

The conventional diffraction techniques being often not satisfactory to locate light atoms such as hydrogen due to their low atomic number and their high thermal vibrations [2], solid-state Nuclear Magnetic Resonance (SSNMR) can be a powerful tool to solve such a problem. Both hydroxyl groups (BAS and silanols) were the subject of several spectroscopic investigations to identify, localize or quantify them. ²⁷Al, ²⁹Si, ¹H SSNMR and infrared spectroscopy were the most used techniques. However, the overlapping of the corresponding signals hinders precise interpretations. The limitations encountered are intrinsic to each technique, both spectroscopies suffer from a low resolution because of the occurrence of strong couplings and hydrogen bonds [3]. Either the isotropic chemical shifts in NMR or the wavenumber frequencies of the O-H bonds in infrared spectroscopy are varying in small ranges reaching the limits nowadays to give new insights on the hydrogen environments in zeolites [4,5].

Several types of defects have been identified in the zeolite frameworks as shown in Figure 1. They include silanols coming from hydrolyzed Si–O–Si bridges; generated by missing tetrahedral framework atoms and those present on the external surface [6]. In addition, siloxy defects (SiO^-) were identified. They exist in the as-synthesized materials to balance the positive charge of the organic structure directing agents (OSDA). In these defects, either pairs or triads, the valence of the oxygen atom is approximately equal to one instead of two for Si–O–Si bridges and thus they are stabilized by a $\text{SiO}^- \dots \text{HOSi}$ hydrogen bond [7]. Furthermore, the electronic density of the oxygen involved in a hydrogen bond depends on the O...H donor-acceptor distance. Its length was estimated to be 1.7 Å using the empirical correlation between the OH bond length and the proton (¹H) NMR chemical shift (10.2 ppm). This increases the electronic density of the oxygen atom but is still not enough to neutralize the system and additional positive charges are needed [8].

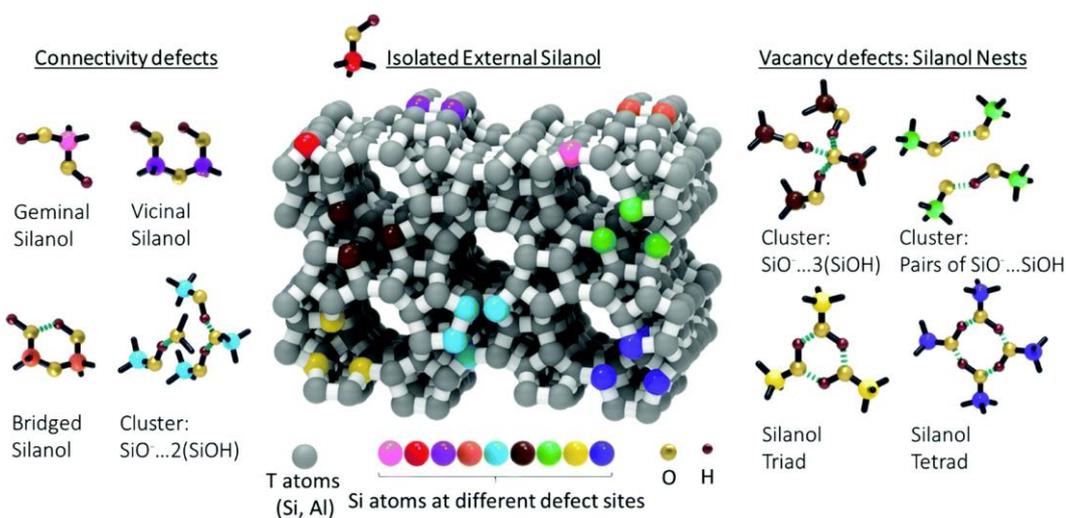


Figure 1. Schematic representation of different types of silanols grouped into three main categories: isolated external silanols, connectivity defects and vacancy defects. Green dotted lines indicate hydrogen bonding [1].

The present contribution presents the role of the OSDA in the positioning and orientation of the siloxy/silanol defects in pure silica zeolite using SSNMR and DFT calculations. Indeed, understanding the interactions between the OSDA and defects in zeolites is a necessary step toward a rational control of their distribution, and to subsequently use this knowledge for positioning catalytic sites using heteroatom substitutions.

EXPERIMENTAL

The following molar composition of the precursor suspensions were used for the synthesis of silicalite-1 samples with MFI type framework structure: 1.0 SiO₂: 0.24 SDA: 20 H₂O. In a typical synthesis, 5.0 g of tetraethyl orthosilicate (TEOS) was added to the corresponding weight of structural directing agents (SDA: methyltributylammonium hydroxide (MeTrBAOH) and tetrapropylammonium (TPAOH)) and 3.95 g of water under stirring at room temperature (pH = 12). The obtained water-clear suspensions were stirred for 3 h at room temperature and further hydrolyzed for 4 h on an orbital shaker. The final suspensions were subjected to hydrothermal treatment at 363 K for 8 h. After crystallization, the nanometer-sized silicalite-1 crystals were purified by high-speed centrifugation (20000 rpm, 20 min). The obtained solid product was washed with hot doubly deionized water (heated at 343 K for 30 min) till the pH reaches 7.5. The nanometer-sized silicalite-1 crystals were subjected to freeze drying in order to prevent irreversible agglomeration. The freeze-dried samples were calcined at 823 K (heating rate 2 K/min) in air for 6 h. The samples synthesized with TPA and MeTrBA are abbreviated as TPA-silicalite-1 and MeTrBA-silicalite-1, respectively. One and two dimensional ¹H magic-angle spinning (MAS) NMR spectra were acquired at 500.07 MHz on a Bruker Avance III-HD (11.7 T), using 1.9-mm outer diameter probes zirconia rotors spun at 40 kHz, a radiofrequency power of 100 kHz and a recycle delay of 2s. The recoupling of the DQ coherence was performed following the BaBa pulse sequence. The incremented delay in the indirect dimension (δt_1) is equal to 50 μ s (i.e., two times the rotor spinning period). The DFT calculations were performed with ORCA, an Ab Initio, DFT and Semiempirical electronic structure package (vers. 4.1.2) [11], with hybrid gradient-corrected PBE0 exchange-correlation functional. Geometry optimization was performed with def2-SVP basis set with utilization of def2/J auxiliary basis.

RESULTS AND DISCUSSION

The symmetry of the (MeTrBA) OSDA is changed with respect to TPA cation keeping the mass of the molecule as close as possible to the TPA, as well as the total number of carbon

atoms. In parallel, pure silicate-1 (MFI) using TPA as OSDA was prepared as a reference sample. MFI was chosen as it presents two different types of channels, in which previous works have shown that alkyl chains of the OSDA may have preferential orientation and therefore, it is a good candidate to evidence possible change in the defect locations depending on the OSDA structure and symmetry [12].

The Figure 2 shows the conventional and the 2D DQ/SQ ¹H MAS NMR spectra of both the as-synthesised TPA-silicalite-1 and MeTrBA-silicalite-1 zeolites displaying a group of resonances between 1.0 and 4 ppm assigned to the protons of the TPA and MeTrBA cations. The isolated peak at 10.2 ppm present in both cases is attributed to the SiO⁻ . . . HOSi defects. In both cases, the principal information given by this experiment is the presence of the correlation (shown by the dashed lines) observed between the siloxy/silanol defects at 10.2 ppm and the protons from the terminal methyl groups in the propyl and butyl chains of the TPA and MeTrBA cations, respectively. In the particular case of MeTrBA-silicalite-1, it is interesting to note that no cross-peak resulting from the interaction between the methyl protons of the isolated methyl group (3 ppm) and the ones present in the butyl chains (1 ppm) is observed, nor between the isolated methyl group and the defects.

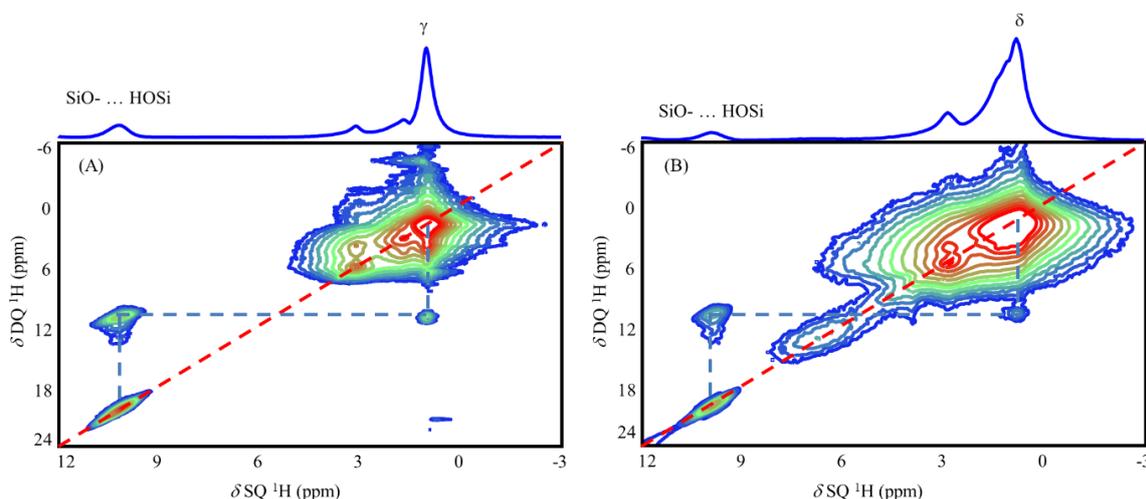


Figure 2. 1D and 2D DQ/SQ correlation ¹H NMR spectra of the as synthesized (left) TPA-silicalite-1 and (right) MeTrBA-silicalite-1 recorded at 500 MHz [10].

These observations can be interpreted as follows: the defects are definitely in the close vicinity of the terminal methyl groups of the longer chains (propyl or butyl) in both samples. Such a conclusion was already delivered in the case of the TPA cation. [9] However the present observations for the MeTrBA-silicalite-1 show clearly the general tendency of the siloxy/silanol defects to be always located near the end of the longer chains. Considering that the positive charge of the alkyammonium is mainly carried by the nitrogen atom, the present results show that the negative charge of the defects are situated as far as possible from the nitrogen atoms. This can be understood by considering that this arrangement is optimal to minimize the whole crystal electrostatic energy.

However, it has been shown for non-symmetric alkyl ammonium, there is a preferential orientation of the alkyl chains in the channels. For instance, the butyl chains have a preferential orientation toward the sinusoidal channels. Therefore, for TPA, with one molecule per intersection, all channels must contain a propyl chain. The fact that the silanol groups are close to the terminal methyl groups of these propyl chains show that the defects are mostly located in the middle of the channels. There is no evidence that these defects may occupy preferentially

either the straight or sinusoidal channels, and therefore the defects are most likely randomly parted between the two possible positions.

The arrangement is different in the case of silicalite-1 synthesized with MeTrBA (sample MeTrBA-silicalite-1) because the butyl chains should be preferentially oriented in the sinusoidal channels, and hence the methyl is expected to point toward the linear channels. Moreover, the steric constraints must favour the location of two butyl chains in the longer sinusoidal channel, instead of the linear channels. Considering these arguments, we expect that the MeTrBA cations are ordered in the channels, with two butyl groups in the sinusoidal and one butyl and one methyl group in the linear channels. Consequently, as the defects are located close to the terminal methyl of the butyl groups, they are most probably located in the sinusoidal channels.

CONCLUSION

In conclusion, the location of the siloxy/silanol (SiO-...HOSi) may be tuned during hydrothermal synthesis by changing the symmetry of the OSDA. It was shown that preferential location of these defects is near the terminal methyl groups of the longer alkyl chains, and thus far from the nitrogen atoms. We postulate based on the preferential orientation of the alkyl groups in the various channels of the MFI structure, that in the case of the non-symmetric MeTrBA template, they are located in the sinusoidal channels, while for the symmetric TPA template they can be randomly distributed among the two types of channels. This work shows that a careful choice of the OSDA agent may be a means to induce a preferential location of the defects in the structure, which can be evidenced by 2D DQ/SQ correlation ¹H NMR spectroscopy. Finally, it can be anticipated that such approach might be the way to control the position of the active sites, for example, in acid zeolite catalysts.

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